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Title of Invention: Two-layer solid electrolyte

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Simple Explanation of Drawings:

Fig. 1 is a cross sectional view of the 2-layer solid electrolyte of this invention; Fig. 2 is an explanatory drawing of a fuel cell using the 2-layer solid electrolyte of this invention; Fig. 3 is a drawing comparing the properties of fuel cells using the 2-layer solid electrolyte of this invention and a conventional single-layer solid electrolyte.

Detailed Explanation of Invention:

This invention concerns a solid electrolyte which is used in fuel cells.

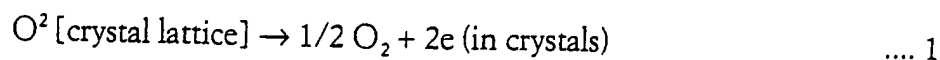
Up to now, as solid electrolytes for use in fuel cells, ones using ZrO_2 as the principal ingredient, such as $\text{ZrO}_2\text{-Y}_2\text{O}_3$ solid solutions (referred to below as " ZrO_2 -based solid electrolytes") and ones using CeO_2 as the principal ingredient, such as $\text{CeO}_2\text{-Gd}_2\text{O}_3$, -MgO and $\text{CeO}_2\text{-Sm}_2\text{O}_3$, -MgO solid solutions (referred to below as " CeO_2 -based solid electrolytes") have been known. The former have the drawback that they have large specific resistances and cannot be used unless the temperature is high, about 1000°C , and the latter have low specific resistances and can be used at temperatures around 700°C , but they have the drawbacks that they have oxygen ion transport numbers which are higher than those of the former ones and the efficiencies of the fuel cells are reduced.

This invention has the purpose of providing solid electrolytes for fuel cells which take advantage of the small specific resistance properties of CeO_2 -based solid electrolytes, but avoid the phenomenon of reduced transport numbers which is a drawback of these electrolytes, and operate efficiently at temperatures around 700°C .

The solid electrolytes of this invention are characterized by the fact that they are composed of 2 layers, using CeO_2 -based solid electrolytes as their bases and covering them with a thin layer of a solid electrolyte which is stable in reducing atmospheres.

CeO_2 -based solid electrolytes have a transport number of their oxygen ions of 1, in an oxidizing atmosphere such as oxygen or air, but when they are used in fuel cells, they are necessarily partially in contact with a reducing atmosphere, such as hydrogen,

and a reaction of the form



The electrons produced as a result induce an electronic conduction, and the transport number becomes smaller. In other words, the following phenomenon occurs. At 800°C, in ZrO₂-based solid electrolytes, the electron conductivity does not become predominant unless the oxygen partial pressure becomes close to 10⁻³⁰ atm; at oxygen partial pressures greater than this, they are substantially ion conductors. In contrast, with CeO₂-based solid electrolytes, the electron conductivity becomes larger than the ion conductivity at an oxygen partial pressure of about 10⁻²⁰ atm. Therefore, in batteries which use CeO₂-based solid electrolytes, the open-circuit voltages are 0.80-0.90 V, lower than the theoretical value of 1.0 V. Furthermore, in CeO₂-based solid electrolytes, the Gd₂O₃, Sm₂O₃, etc., are added in order to increase the ion conductivity, and the addition of the MgO is for the same reason, as well as the reason that it lowers the sintering temperature. However, the drawbacks mentioned above remain.

In this invention, in order to prevent this reduction of the transport number, the parts of the CeO₂-based solid electrolyte sintered bodies which are in contact with reducing atmospheres are covered by a thin film of a solid electrolyte which is stable in reducing atmospheres, i.e., does not undergo primary reactions. This solid electrolyte of this invention is shown in Fig. 1. In this figure, 1 is the 2-layer solid electrolyte of this invention, 1a is a CeO₂-based solid electrolyte sintered body, and 1b is a solid electrolyte thin layer which is stable in reducing atmospheres, composed of a ZrO₂, ThO₂, etc., substrate, for example, coated on this sintered body by the chemical deposition method, sputtering method, etc. The 1a side is used in an oxidizing atmosphere, and the 1b side in a reducing atmosphere.

The CeO₂-based solid electrolytes, since they have small specific resistances, do not have large resistances even if they are made quite thick, in order to have mechanical strength; therefore, even if they are coated with a thin layer of a solid electrolyte with a large specific resistance, the resistance as a whole does not become large. Therefore, one

can obtain solid electrolytes with large mechanical strengths and small electrical resistances.

In the make-up described above, also, it is clear from the following argument that the resistance of the whole solid electrolyte is almost unchanged from the CeO_2 -based solid electrolyte used as the substrate.

In Fig. 1, if the specific resistance of the CeO_2 -based solid electrolyte 1a is ρ_1 , the specific resistance of the coated solid electrolyte 1b is ρ_2 , their respective thicknesses are d_1 and d_2 , the specific resistance ρ of the 2-layer solid electrolyte 1 composed of both of them is given by

$$\rho = \left(\frac{d_1}{d_1 + d_2} \right) \rho_1 + \left(\frac{d_2}{d_1 + d_2} \right) \rho_2 \quad \dots 2$$

where, since ρ_1 and ρ_2 are $15 \, \Omega \text{ cm}$ and $75 \, \Omega \text{ cm}$, respectively, at about 700°C , ρ can be made almost equal to ρ_1 by taking d_2 sufficiently small, compared with d_1 , e.g., $d_2/d_1 = 1/100$, approximately.

Next, this invention will be explained in detail by means of working examples.

Working Example 1

Seven moles cerium oxide powder (CeO_2), 3 moles gadolinium oxide (Gd_2O_3), and 0.3 mole magnesium oxide (MgO) were thoroughly mixed and molded by means of a press in a circular plate shape. After this, the molding was sintered in air at 1800°C , and a dense sintered circular plate 1a with a thickness of 0.04 cm was obtained. This product was put into a quartz tube and the tube was heated to approximately 800°C . A mixed ($\text{H}_2 + \text{CO}_2$) gas containing ZrCl_4 and YCl_3 in the ratio of 10:1 was passed through the tube, as a carrier gas, for approximately 10 minutes, and a $\text{ZrO}_2\text{-Y}_2\text{O}_3$ layer 1b with a thickness of approximately 1 micron was formed on the CeO_2 -based solid electrolyte sintered body to obtain a 2-layer solid electrolyte 1.

Working Example 2

Silver electrodes 2 and 3 were placed on both sides of the 2-layer solid electrolyte 1 obtained in Working Example 1 by the paste method, etc., and platinum leads 4 and 5 were connected to these silver electrodes 2 and 3 by a suitable method. This 2-layer electrolyte circular plate 1 with silver electrodes attached was adhered to the center of a heat-resistant insulating tube made of alumina, etc., to obtain a fuel cell.

A certain part of the electrolyte circular plate 1 of the aforementioned heat-resistant insulating tube 6 was heated from the outside to approximately 750°C by a suitable heat source. Air was passed over the CeO_2 -based solid electrolyte 1a side in the tube 6, and hydrogen was passed over the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ solid electrolyte thin film 1b side, as a carrier gas; the voltage-current characteristic was measured by using leads 4 and 5. The results are shown as curve 1 in Fig. 3. For comparison, the results of the same measurement performed on a fuel cell with the same structure as in Fig. 2, using a solid electrolyte circular plate of the conventional type, with a $\text{CeO}_2\text{-Gd}_2\text{O}_3\text{-MgO}$ single layer, are shown as curve 2.

From this figure, it is clear that the fuel cell made with the 2-layer solid electrolyte of this invention has superior properties to those of the conventional fuel cell made with the single-layer solid electrolyte.

Working Example 3

While a tubular body made of a $\text{CeO}_2\text{-Sm}_2\text{O}_3\text{-MgO}$ solid electrolyte, 0.01 cm thick, was heated to approximately 700°C , a mixed ($\text{H}_2 + \text{CO}_2$) gas containing ThI_4 and YCl_3 in the ratio of 10:1 was passed through the tube. In the same manner as in Working Example 1, an electrolyte tube composed of 2 layers, with a $\text{ThO}_2\text{-Y}_2\text{O}_3$ solid electrolyte thin film approximately 1 micron thick on the inside of the aforementioned tubular body, was obtained.

Silver electrodes were adhered to the inner and outer sides of this 2-layer electrolyte tube by deposition, etc., and hydrogen was allowed to flow over the inside of this

tube, while fuel gas was allowed to flow over its outside; a fuel oil with good properties, as in Working Example 1, was obtained.

As is clear from the explanation given above, fuel cells formed from the 2-layer solid electrolyte of this invention have smaller reductions in their oxygen ion transport numbers than those made with the conventional single layer solid electrolytes, and they operate efficiently at suitable temperatures, about 700-900°C. Therefore, they have a great practical effectiveness.

Claims:

- 1 A 2-layer solid electrolyte, characterized in that it uses a CeO_2 -based solid electrolyte as the substrate, and a thin film of a solid electrolyte which is stable in a reducing atmosphere is adhered on top of it.

Fig. 1

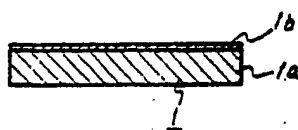


Fig. 2

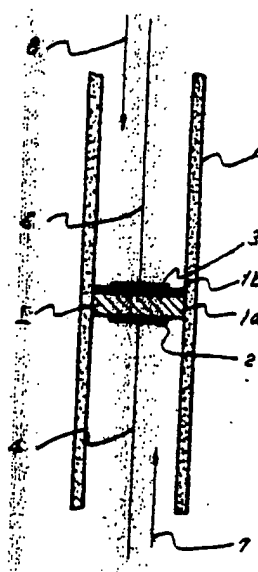
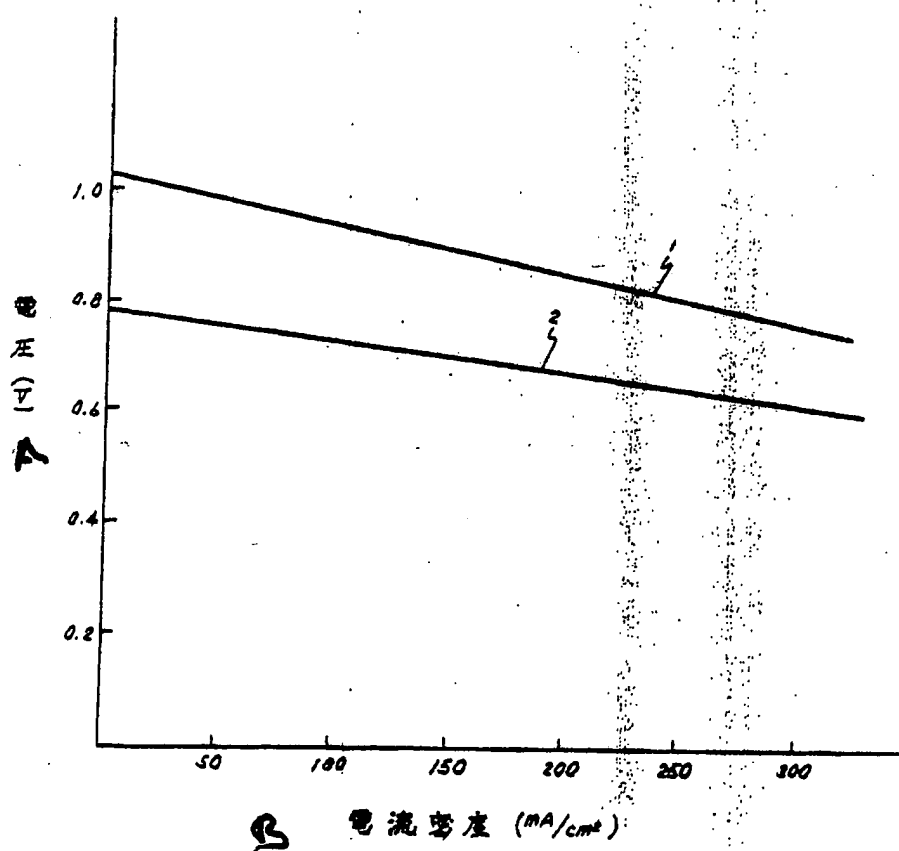


Fig. 3



a. Voltage (V)

b. Current density (mA/cm²)

特 許 公 報

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⑤ 2層固体電解質

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⑦ 出 願 昭45(1970)1月5日

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図面の簡単な説明

第1図は本発明の2層固体電解質の断面図、第2図は本発明2層固体電解質を用いた燃料電池の説明図、第3図は本発明2層固体電解質を用いた燃料電池と従来の単層固体電解質を用いた燃料電池の特性比較図である。

発明の詳細な説明

本発明は燃料電池に用いられる固体電解質に関する。

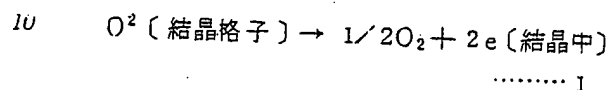
従来、燃料電池用の固体電解質として $ZrO_2 - Y_2O_3$ 固溶体等の ZrO_2 を主成分とするもの(以下 ZrO_2 基固体電解質と称する)と、 $CeO_2 - Gd_2O_3 - MgO$ 、 $CeO_2 - Sm_2O_3 - MgO$ 固溶体等の CeO_2 を主成分とするもの(以下 CeO_2 基固体電解質と称する)とが知られている。前者は比抵抗が大きく、1000℃程度の高温にしないと用いられない欠点があり、後者は前者より比抵抗が小さく、700℃程度で用いることができるが、酸素イオンの輪率が前者より小さく、燃料電池の効率を小さくする欠点がある。

本発明は CeO_2 基固体電解質の小さい比抵抗特性を生かしながら、その欠点である輪率低下現象を防ぎ、700℃程度の温度で効率よく作動する燃料電池用の固体電解質を提供することを目的とする。

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本発明の固体電解質は CeO_2 基固体電解質体を基体とし、その上に還元性雰囲気中で安定な固体電解質の薄層を被着した2層からなることを特徴とする。

5 CeO_2 基固体電解質は酸素あるいは空気のような酸化性雰囲気中では、その酸素イオンの輪率は1であるが、燃料電池に用いられるときは、その一部分は必然的に水素のような還元性雰囲気に触れ



なる反応が起り、その結果生じた電子によつて電子性の導電が誘起され、その輪率が小さくなるものである。以上のことをいふとすれば次の通りである。

15 ある。すなわち、800℃において、 ZrO_2 基固体電解質では酸素分圧が 10^{-30} atm、付近にしないと電子導電性が支配的にならず、それ以上の酸素分圧では本質的にイオン導電体である。これに対して、 CeO_2 基固体電解質では 10^{-20}

20 atm、の酸素分圧で電子導電性がイオン導電性より大になる。そのため、 CeO_2 基固体電解質を用いた電池では、開路電圧は0.80~0.90Vで、理論値の1.0Vより低くなるということである。

なお、 CeO_2 基固体電解質において、 Gd_2O_3 、 Sm_2O_3 等が添加されているのはイオン導電性を増加させるためであり、また、 MgO の添加は上記と同じ理由であるが、このほかに焼結温度を低下させる効果もあるためである。しかし、なお上記の欠点をもっているものである。

30 この輪率の低下を防ぐために本発明においては、 CeO_2 基固体電解質焼結体の還元性雰囲気に触れる部分を、還元性雰囲気に安定な、すなわち、1式の反応が起らないような固体電解質の薄層で被覆するものである。上記本発明固体電解質を第1図に示す。図において、1は本発明の2層固体電解質、1aは CeO_2 基固体電解質焼結体、1bはその上に化学蒸着法、スパッタ法等によつて被

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着した例えば ZrO_2 基、 ThO_2 基等からなる還元性雰囲気中で安定な固体電解質薄層であり、1a側を酸化性雰囲気、1b側を還元性雰囲気として使用する。

CeO_2 基固体電解質は比抵抗が小さい関係で、機械的強度を持たせるために充分厚くしても抵抗は大きくならないので、その上に比抵抗の大きな固体電解質の薄層を被着しても全体としての抵抗は大きくならず、したがって、機械的強度が大で、しかも電気抵抗の小さな固体電解質が得られる。

上記のような構成にしても固体電解質全体の抵抗が基体となる CeO_2 基固体電解質とほとんど変わらないことは下記の点からも明らかである。

すなわち、第1図において、 CeO_2 基固体電解質1aの比抵抗を ρ_1 、被着した固体電解質1bの比抵抗を ρ_2 、それぞれの厚さを d_1 、 d_2 とすれば、両者からなる2層固体電解質1の比抵抗 ρ

$$\rho = \left(\frac{d_1}{d_1 + d_2} \right) \rho_1 + \left(\frac{d_2}{d_1 + d_2} \right) \rho_2$$

で与えられる。ここで、 ρ_1 および ρ_2 は $700^\circ C$ 程度でそれぞれ $15 \Omega cm$ 、 $75 \Omega cm$ であるから、 d_1 に対して d_2 を例えば $d_2/d_1 = 1/100$ 程度に充分小さくすることによつて ρ を ρ_1 とほとんど等しくすることが可能である。

次に本発明を実施例につき詳細に説明する。

実施例 1

粉末の酸化セリウム (CeO_2) 7モル、酸化ガドリウム (Gd_2O_3) 3モル、酸化マグネシウム (MgO) 0.3モルを十分に混合し、円板状にプレス、成型した後、空气中 $1800^\circ C$ で焼結して厚さ $0.04 cm$ の微密な焼結円板1aを得る。これを石英管中に入れ、この管を約 $800^\circ C$ に加熱し、ここに ZrO_2 、 Y_2O_3 を $10:1$ の割合で含んだ ($H_2 + CO_2$) 混合ガスを担体ガスとして約10分間通じると、厚さ約1ミクロンの $ZrO_2 - Y_2O_3$ 層1bが CeO_2 基固体電解質焼結円板上に形成され、2層電解質円板1が得られる。

実施例 2

実施例1で得た2層電解質円板1の両面にペー

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銀電極2および3に適当な方法により白金等のリード線4および5を接続する。この銀電極をつけた2層電解質円板1をアルミナ等からなる耐熱絶縁管6の中にアルミナセメント等で接着すれば、

5 燃料電池が得られる。

前述の耐熱絶縁管6の電解質円板1のある部分を外部から適当な熱源によつて約 $750^\circ C$ に加熱し、管6中の CeO_2 基固体電解質1a側には空気を、 $ZrO_2 - Y_2O_3$ 固体電解質薄層1b側には燃料ガスとして水素を流し、リード線4および5によつてその電圧-電流特性を測定した。その結果を第3図に曲線1で示した。同図には比較のために、従来の $CeO_2 - Gd_2O_3 - MgO$ 単層の固体電解質円板を用いた第2図と同一構造の燃料電池について同様な測定を行なつた結果を曲線2で示した。

同図から、本発明の2層固体電解質からなる燃料電池は従来の単層固体電解質からなる燃料電池より特性が優れていることは明らかである。

20 実施例 3

厚さ $0.01 cm$ の $CeO_2 - Sm_2O_3 - MgO$ 固体電解質からなる管状体を約 $700^\circ C$ に加熱しながらその内部に ThI_4 と YCl_3 の $10:1$ で含んだ ($H_2 + CO_2$) の混合ガスを流すと、実施例1と同様に前記管状体の内面に厚さ約1ミクロンの $ThO_2 - Y_2O_3$ 固体電解質薄層をもつた2層から電解質管ができる。

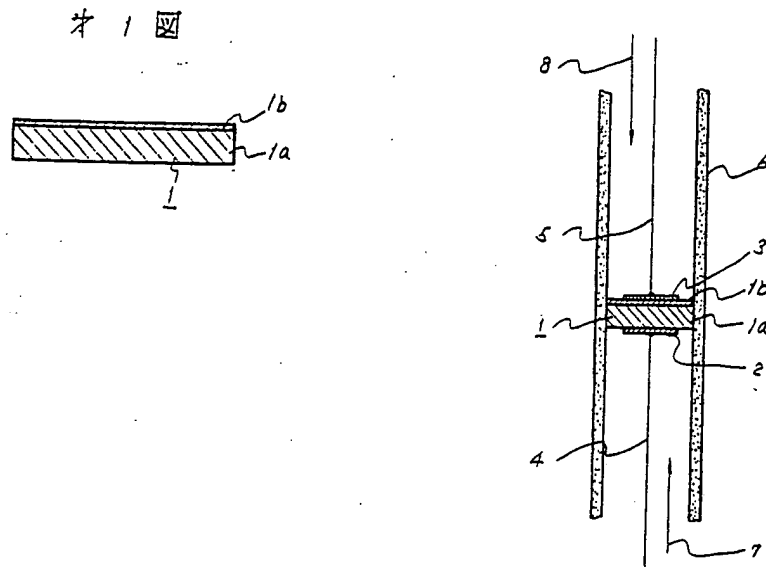
この2層電解質管の内外面に蒸着等によつて銀電極を被着し、この2層電解質管の内側に水素を外側に燃料ガスを流すようにすれば実施例1と同様に特性のよい燃料電池が得られる。

以上の説明から明らかなように、本発明の2層固体電解質で構成された燃料電池は従来の単層固体電解質で構成されたものに比べ酸素イオン輸率の低下が少なく、 $700 \sim 900^\circ C$ 程度の適当な温度で効率よく作動するので実用上の効果顕著である。

⑥特許請求の範囲

1 CeO_2 基固体電解質体を基体とし、その上に還元性雰囲気中で安定な固体電解質の薄層を被着してなることを特徴とする2層固体電解質。

才 2 図



才 3 図

